SCIENCE FOR GLASS PRODUCTION

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METHODS FOR OBTAINING PROTECTIVE ATMOSPHERES USED IN FLOAT-GLASS PRODUCTION (REVIEW)

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Based on the analysis of patent information, the scientific and technical literature, and research performed at the Saratov Institute of Glass, a classification is proposed for the types of protective nitrogen-hydrogen atmosphere depending on methods of its production. The methods are considered, and the main methods for gas refinement from impurities are listed. A comparative analysis of the methods for producing protective atmospheres is carried out, and the advantages and disadvantages of each method are discussed.

One of the main factors preventing oxidation of tin in the course of glass formation on molten tin is the use of a protective atmosphere. The requirements imposed on such an atmosphere are especially stringent. Most patents describe the use of a nitrogen-hydrogen gas atmosphere with different hydrogen contents. For instance, the atmosphere supplied to the front part of the melting tank contains 2 – 8% hydrogen (here and elsewhere vol.%), and the atmosphere supplied to the exit part contains 3 – 10% (Gr. Britain Patent No. 1034322, French Patent No. 1376823). An essential factor here is profound refinement of the protective atmosphere from oxygen, whose content should not exceed 0.0001%. The admissible H_2O impurity should not exceed the content corresponding to a dew point of – 60 or – 70°C, and the content of CO_2 and SO_2 should not exceed 0.0001%. The known classification of the types of protective atmosphere [1] is based on the composition of gas mixtures reacting with metals. Based on this main principle, four types of protective atmosphere are distinguished:

$H_2 – H_2O – N_2$;
$CO – CO_2 – N_2$;
$CO – CO_2 – H_2 – H_2O – N_2$;
$CO – CO_2 – H_2 – CH_4 – N_2$.

A protective atmosphere is widely used in metallurgy and machine-building for thermal and chemicothermal treatment of metals and alloys.

One of the most effective types of protective atmosphere used in the glass industry is a nitrogen-hydrogen mixture with 85 – 96% N_2 and 4 – 15% H_2 and a minimum content of oxygen, water vapor, and other impurities. Such an atmosphere is universal in industrial practice and is used for thermal treatment within a wide temperature range: from 200 to 1200°C.

Both domestic and foreign float-glass manufacturers are confronted with the problem of choosing the most effective method for developing a protective nitrogen-hydrogen atmosphere with the minimum possible impurity content. Based on the literary data, we made up a classification of types of nitrogen-hydrogen atmospheres based on the methods of their production (Scheme 1). This classification principle fully agrees with the above-mentioned main principle of classification. It should also be noted that the classification includes only methods for production of a nitrogen-hydrogen atmosphere used in Russia. Let us consider these methods in detail.

Production of a protective atmosphere from hydrocarbon gases [2, 3] implemented through partial combustion of these gases with variable air-excess coefficient and using the gas-generation process.

In the first case, either an endothermic or an exothermic atmosphere can be obtained.

To produce an endothermic atmosphere, the plant uses the principle of partial combustion of hydrocarbon gases with an air-excess coefficient of about 0.25. The initial material can be natural gas, liquefied propane-butane mixture, or other hydrocarbon gases. If the initial gas contains sulfur compounds, it is preliminarily passed via the retort of a sul-

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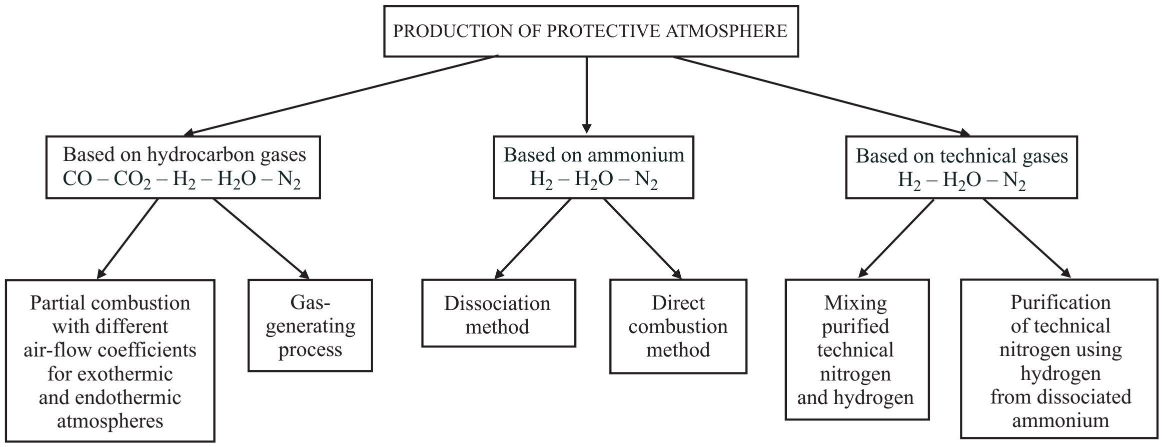

Scheme 1

fur-refining chamber heated to 350°C and filled with the sulfur absorbent GIAP-10.

Based on the experimental data, one can assume that the process of generating endothermic gas, which contains up to 20.5% CO, up to 40% H_2, and the rest N_2, in accordance with the reaction

$$CH_4 + 0.5O_2 = CO + 2H_2,$$

is implemented in two stages. At the first stage, nearly complete combustion of methane takes place in accordance with the reaction

$$0.5CH_4 + O_2 = 0.5CO_2 + H_2O,$$

which is accompanied by a temperature increase and the formation of substantial quantities of carbon dioxide and water vapor. The second stage of the process is mainly characterized by the endothermic reactions of methane to earlier formed water vapor and carbon dioxide (conversion of methane). The respective reactions are as follows:

$$CH_4 + H_2O = CO + 3H_2;$$

$$0.5CH_4 + 0.5CO_2 = CO + H_2.$$

To produce an exothermic atmosphere, the plant uses the principle of partial combustion of hydrocarbon gases with an air-excess coefficient of about 0.6 – 0.9. The initial material can be natural gas or liquefied propane-butane mixtures.

The ÉPKS-4000 production line uses an exothermic nitrogen-hydrogen protective atmosphere. The plant consists of four units:

– combustion (high-temperature incomplete combustion of natural gas);

– conversion (low-temperature vapor conversion of carbon monoxide);

– chilling (chilling of combustion products and separation of drop moisture);

– adsorption purification and drying (short-cycle adsorption purification of combustion products from moisture and carbon dioxide).

In this way, the following composition of protective atmosphere is obtained (%): 0.5 – 20 H_2, 0.0001 O_2 (high-purity gas mixture), 0.00106 H_2O (or – 60°C dew point), up to 0.05 CO_2, up to 0.05 CO, and the rest N_2 . The microimpurities (≤ 0.0001%) in the mixture may include residual CH_4 and NO.

This method for the production of a protective atmosphere was developed at the Saratov Institute of Glass (USSR Inventor's Certif. No. 863511) [4] and patented in Great Britain, France, and West Germany.

It should be noted that the production technology for an exothermic atmosphere is simpler and more economical than that for an endothermic atmosphere.

Let us consider the gas-generation process [1]. This is a standard process with different degrees of purification from H_2S and CO_2 and drying. The following protective atmosphere is obtained (%): 5 – 15 H_2, – 40 to + 20°C dew point of H_2O, 0.1 – 6.0 CO_2, 25 – 28 CO, 1 – 2 CH_4, and 60 – 65 N_2. As the composition of the resulting protective atmosphere differs from the above-specified composition of effective gas atmosphere, it is not used in float-glass production.

Protective atmosphere based on ammonium [2, 3, 5] can be obtained by dissociation and by direct combustion of ammonium.

A plant generating such a protective atmosphere is based on the principle of ammonium dissociation and subsequent combustion of hydrogen mixed with air. The gaseous ammonium is fed into the dissociator retort, passes through a layer of GK-2 or TsChÉM-I catalysts at a temperature of 700 – 800°C, and dissociates into nitrogen and hydrogen, according to the reaction

$$2NH_3 \rightarrow N_2 + 3H_2.$$

Next, the nitrogen-hydrogen mixture via the evaporator coil and the pipe chiller is fed into the combustion chamber

and burned to the required hydrogen content. In this case, the hydrogen content in the resulting gas can range from 4 to 20%.

The protective atmosphere obtained by ammonium dissociation has the best composition and purity (absence of impurities); however, it required an extremely complicated technology and sophisticated machinery.

The plants for producing protective atmosphere by direct combustion of ammonium are also based on the principle of dissociation and subsequent burning of hydrogen mixed with air. However, a new catalyst developed and tested in Russia made it possible to combine the specified processes:

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O;$$

$$2NH_3 \rightarrow N_2 + 3H_2;$$

$$H_2 + 0.5O_2 = H_2O.$$

Catalysts of the TsChÉM-III group are produced by impregnation of granulated active aluminum oxide with a solution containing ammonium dichromate and sodium and nickel nitrates, with subsequent calcination. The use of this catalyst made it possible to simplify the technology of obtaining a controlled protective atmosphere and to combine the equipment for ammonium dissociation and additional burning of hydrogen into a single unit, i.e., a chamber for direct combustion of ammonium.

Production of a controlled protective atmosphere based on technical gases [2, 3, 5] can be implemented by mixing purified technical nitrogen and hydrogen and purification of technical nitrogen using hydrogen from dissociated ammonium.

Plants for producing protective atmospheres via purification of technical gases from oxygen are based on the hydration principle with subsequent drying. The initial gases are technical hydrogen produced by electrolysis of water and technical nitrogen supplied from oxygen stations. The oxygen content after refinement does not exceed 0.0005%, and the hydrogen content in refined nitrogen ranges from 4 to 10%.

There are also plants for producing protective atmosphere containing 90 – 96% N_2 and 4 – 10% H_2 through the refinement of technical nitrogen from oxygen impurities using hydrogen produced by ammonium dissociation with subsequent drying of the atmosphere to a dew point of – 40°C. The initial materials are nitrogen from oxygen stations and liquid ammonium.

Analyzing the above-described methods for the production of a protective atmosphere, it can be concluded that the whole atmosphere-generating process in principle can be reduced to the purification of hydrogen, inert gases, and their mixtures from rather small quantities of oxygen, water vapor, and other impurities that have a negative effect on the main production processes.

In this connection, it is expedient to briefly analyze the main methods for removal of impurities from gas.

Purging gases of oxygen. The following methods found practical application in purging gas of oxygen:

– direct chemical binding of oxygen;

– catalytic binding (the most widely used catalysts in oxygen hydration are spongy copper, iron-copper-nickel, palladium, platinum, and chromium-nickel catalysts);

– diffusion separation through a metal mesh.

Removal of moisture from gases. The processes used for gas drying can be split into three groups:

– chemical binding of water vapor;

– water vapor sorption with solid adsorbents;

– freezing.

Removal of carbon monoxide and dioxide from gases. Two methods for removal of carbon monoxides are used. The choice of the particular method depends on the permissible CO content in the refined gas. Carbon monoxide that has to be removed is converted into CO_2 according to the reaction

$$CO + H_2O = CO_2 + H_2.$$

The first method implies one-stage removal of CO_2, and the second method implies two-stage purification.

Thus, the methods generating protective atmospheres based on hydrocarbon gases do not require expensive equipment and materials and are based on simple technological processes. However, the resulting protective gas contains significant amounts of various impurities (carbon dioxide, methane, sulfur compounds), which calls for the application of expensive catalysts and additional purifying equipment.

The method for producing a protective atmosphere based on dissociated ammonium is technologically complicated, as its consists of two stages: dissociation and additional combustion of hydrogen. This requires a higher energy consumption and additional equipment. The oxygen content in the protective atmosphere after purification does not exceed 0.0005%, and the moisture content after drying correlates with a dew point of – 40°C.

The method based on direct combustion of ammonium has several advantages: simplicity of the technological process and equipment, low electricity consumption, and absence of contaminating impurities in the protective atmosphere.

The method for producing atmosphere based on technical gases is extremely labor-consuming and requires high consumption of electrical power and the presence of expensive palladium catalysts. The protective atmosphere contains water vapor; therefore, it has to be previously dried in a silica-gel drier to a dew point of – 40°C.

Float glass can be produced in a protective atmosphere generated by any of the above-listed methods on condition of additional removal of carbon monoxide and dioxide in the cases where the said components are present in the resulting gas composition.

The float-glass-melting tanks in Russia and the CIS countries are currently using a protective atmosphere generated on the basis of hydrocarbon gases, which was developed at the Saratov Institute of Glass.

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